# REACTIVITY OF COPPER-BASED SORBENTS IN COAL GAS DESULFURIZATION

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## ABSTRACT

The lower temperature range of current practical significance has created a renewed interest in the development of regenerable copper-based sorbents. A unique feature of a copper-based sorbent is its capability to achieve extremely low levels of $H_2S$ in the cleaned fuel gas, provided the sorbent is stabilized against complete reduction to elemental copper. At lower desulfurization temperatures copper-based sorbents can be more effectively stabilized against reduction in the fuel gas environment.

Various combinations of CuO with $MnO_2$, $MoO_3$ were made to prepare sorbents by using a simple mixing method. CuO was used as main active material, $MnO_2$ and $MoO_3$ as additives, and $SiO_2$ as support material. TGA screening and GC/microreactor multi-cycle reactions were carried out to characterize reactivities of sorbents. Sulfidation temperature was 500   and regeneration temperature ranged 500~700  . Through the TGA test, promising sorbents were chosen and tested in GC/microreactor up to the 19th cycle. Sulfur loading was most affected by the ratio of CuO, $MoO_3$ and $MnO_2$. Sorbent containing additves of $MoO_3$ and $MnO_2$ was fully stabilized after the 19th cycle and showed best sulfur loading of 15%.

## INTRODUCTION

Cleaning technology of coal gas in the high temperature is essential for successful development of IGCC. High temperature cleaning technology is classified to two major processes, removing particles process and desulfurization process. Removing particles means removing physical impurities and desulfurization means removing chemical impurities such as $H_2S$ with an effective way [Ryu et al., 1998 ; Ayala et al., 1995 ; Tamhankar et al., 1986 ; Kang et al., 1997].

Most sulfides that exist in coal are converted into $H_2S$ during gasification, and rest of them are converted into $SO_2$ in a turbine. $SO_2$ becomes precursor of acid rain extremely harmful to the ecosystem [Ayala et al., 1995].

Because of recent stringent regulation against air pollution, $H_2S$ in the exit gas should be controlled under several hundreds ppmv in the IGCC system. Therefore, development of sorbents removing $H_2S$ effectively is the key technique in the IGCC. From 1980 to early 1990's, development of metal oxides removing $H_2S$ over 550°C was mainly focused. Recent evaluation of economics for IGCC, however, showed that heat efficiency rapidly increases up to 350°C but in the range of 350~600°C, increment of

heat efficiency is not remarkable. In addition, because of vaporization of alkali metal, it is desirable to operate the process below 650°C [Ryu et al., 1998 ; Abbasian et al., 1997]. Even though efficiency of IGCC increases as operating temperature increases, optimal desulfurization temperature is known to be in the range of 350~550°C because of limitations of equipment and alkali contents in fuel gas. There are several things to be concerned to select sorbents for IGCC; desirable thermodynamic equilibrium, relatively high reactivity, environmental affinity, moderate cost, and so on.

Westmoreland et al. performed desulfurization experiment systematically by using 28 elements and found out 10 elements (Fe, Zn, Mo, Mn, V, Ca, Sn, Ba, Cu, W) are proper as sorbents in the range of 400~1200°C[Westmoreland and Harrison, 1976]. Ayala et al. investigated thermodynamic $H_2S$ equilibrium concentration by doing desulfurization experiment in the temperature range of 350~550°C for the 10 elements chosen in Westmoreland and Harrison's work. Moles of solid oxides and fuel gas during sulfidation were decided based on 50% conversion. As a result, Ayala et al. found that Cu is the worst sorbent among the metals or metal oxides they tested, but CuO can keep $H_2S$ concentration lower than any other sorbents [Ayala et al., 1995].

In this research, several sorbents containing CuO as main active material were prepared. A sequence of sulfidation and regeneration reactions by using the sorbents was performed in the range of 350~550°C. Effects of additives and supports on sulfur loading were also investigated.


## EXPERIMENT

### Sorbent Preparation

$MnO_2$ and $MoO_3$ were chosen as additives and $SiO_2$ was chosen as support material. It is known that $MoO_3$ plays a role of promoter in sulfidation of CuO, and $MnO_2$ inhibits vaporization of Mo in high temperature [Gaper and Washington, 1993].

In our research, we denominated the sorbents that contain $MoO_3$ and $MnO_2$ as CMS sorbents, gave each of them a serial number according to its composition. The ratio of active materials and additives are shown in Table 1. According to the literature, there is no remarkable change of desulfurization efficiency between physically mixed sorbent and sorbent prepared by precise method such as the impregnation and precipitation methods [Kyotani et al., 1989]. Therefore, considering economics and mass production, a simple physical mixing method was employed. CuO, $MoO_3$, $MnO_2$ and $SiO_2$ were mixed in ball mill for 6 hours. EG(ethylene glycol) was added to make it a paste form. The paste was extruded by an extruder like noodles, and then placed on aluminum pan and dried at 200°C for 4 hours. Finally, it was calcinated in a tubular furnace at 700°C for 4 hours, and cooled down, crushed and sieved to a desired size of 92~106μm.

### Experimental Apparatus

A TGA(model 951TA, *Dupont Instrument, Ind*.) was used to investigate weight change of sorbents during sulfidation/regeneration. As shown in Fig. 1, experimental apparatus is largely divided into two parts; TGA and GC/microreactor. Gas flow rate was controlled by MFC(mass flow controller). The simulated gas composition is shown in Table 2.

The mixed gas flows into TGA through the mixing tank. Water is injected before TGA entrance by a syringe pump. Stainless steel pipe from the water injection point to the TGA entrance is wrapped by heating tape to prevent water from condensing.
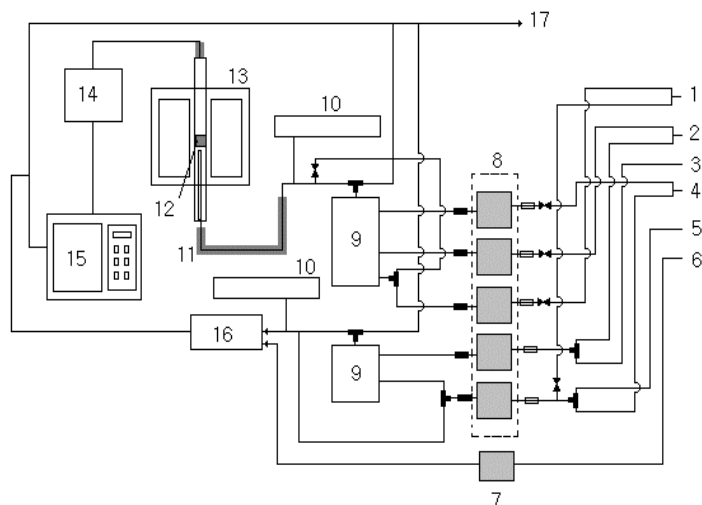


**Fig. 1. Schematic diagram of experimental apparatus.**

| | |
|---|---|
| 1. $N_2$ | 2. $H_2S$ |
| 3. $SO_2$ | 4. Mixing gas |
| 5. Air | 6. $N_2$ |
| 7. Flow meter | 8. MFC |
| 9. Mixing tank | 10. Syringe pump |
| 11. Heating tape | 12. Sample |
| 13. Microreactor | 14. Water trap |
| 15. GC | 16. TGA |

**Table 1. Composition of various sorbents (wt%)**

| Sorbent | $CuO:MoO_3$ $:MnO_2:SiO_2$ | Others : Silica | $CuO:MoO_3$ $:MnO_2$ | Metal Content |
|---|---|---|---|---|
| *CMS1* | 35:13:2:50 | 50:50 | 70:26:4 | 38 |
| *CMS2* | 18:7:1:74 | 26:74 | 71:25:4 | 20 |
| *CMS3* | 16:10:1:73 | 27:73 | 58:40:2 | 20 |
| *CMS4* | 53:19:3:25 | 75:25 | 71:25:4 | 57 |
| *CMS5* | 71:25:4:0 | 100:0 | 71:25:4 | 76 |
| *CMS6* | 64:11:3:25 | 75:25 | 81:15:4 | 61 |
| *CMS7* | 42:30:3:25 | 75:25 | 56:40:4 | 44 |
| *CS1* | 50:0:0:50 | 50:50 | 100:0:0 | 50 |
| *CS2* | 75:0:0:25 | 75:25 | 100:0:0 | 75 |

The flow of mixed gas was vented to a hood until the temperature in the TGA chamber reaches 500 . After the temperature reached to 500 , the mixed gas flowed into the TGA by manipulating valves. After reduction and sulfidation reactions, the TGA system was purged by $N_2$ gas. Then, TGA temperature was set to 700 which is same as the regeneration temperature. After the temperature reached to 700 regeneration gas flowed into the TGA. As described above, a cycle of sulfidation and regeneration was repeated.

GC used in this research is a YoungIn M600D model(*Young-In. Ind.*) in which TCD detector is attached.

**Table 2. Composition of simulated gas**

| Sulfidation | |
| --- | --- |
| $H_2$ | 30.7 vol% |
| $CO_2$ | 6.8 vol% |
| $H_2S$ | TGA:0.28 %, GC:1 vol% |
| $H_2O$ | 10.8 % |
| $N_2$ | Balance |
| Regeneration | |
| $O_2$ | 5% |
| $N_2$ | Balance |

Microreactor was made of quartz tube of 1 inch diameter which has stratum for quartz wool to support sorbents. Composition of simulated gas for GC/microreactor experiment was same as for that of TGA experiment. A small refrigerator was used to remove water in the exit gas from the microreactor.

## RESULTS AND DISCUSSION

**Sulfidation/Regeneration mechanism**

Weight change of CMS1 sorbent during sulfidation/regeneration is shown in Fig. 2. Reaction temperature of sulfidation/regeneration was 500 . By analyzing the weight change, tentative mechanism of sulfidation and regeneration was obtained. Because reduction and sulfidation reactions occur simultaneously in desulfurization process, it is very difficult to know how much reduction reaction affects sulfidation reaction. Therefore, in this research, sulfidation was carried out after reduction was completely finished with $H_2/N_2$ gas. Without considering the effects of additives such as $MoO_3$ and $MnO_2$, we inferred that CuO be converted into Cu by $H_2$ and Cu into $Cu_2S$ by $H_2S$. If Cu was fully converted into CuS, the weight recovery during reduction would reach to twice of the weight loss during the sulfidation.

① reduction
$CuO + H_2$ $Cu + H_2O$
② sulfidation
$2Cu + H_2S$ $Cu_2S + H_2$
③ regeneration

$$2Cu_2S + 4O_2 \quad CuSO_4 + 2CuO + SO_2$$

④ reduction (2nd cycle)

$$H_2 + CuO \quad Cu + H_2O$$

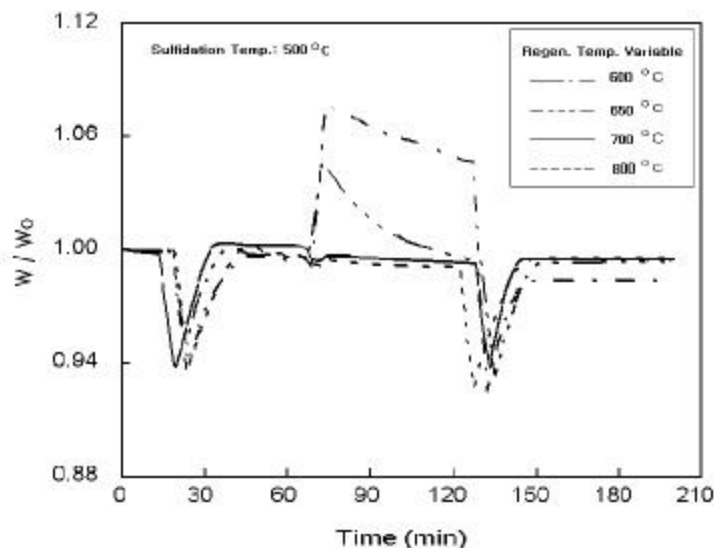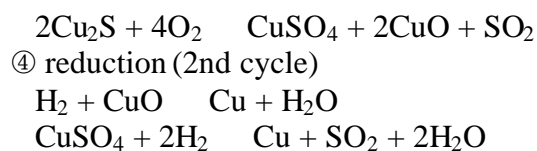$$CuSO_4 + 2H_2 \quad Cu + SO_2 + 2H_2O$$



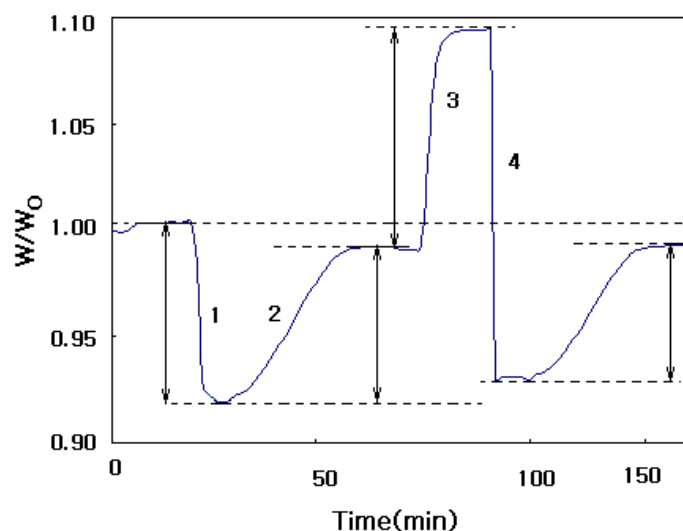**Fig. 2. Result of sulfidation/regeneration using TGA (CMS1, 1.5cycle).**



**Fig. 3. Effects of regeneration temperature on sulfate decomposition (CS1).**

The above reaction mechanism was constructed only based on the weight change of the sorbent. Weight gain during the regeneration is same as weight loss recovery during the sulfidation. It is expected that weight gain during regeneration is caused by sulfate formation. Actually, $CuSO_4$ is the most stable form in the regeneration gas atmosphere at 550 [Ayala et al., 1995].

**Effects of Regeneration Temperature**

Effects of regeneration temperature on sulfate formation are shown in Fig. 3. CS1 sorbent consisted of CuO and $SiO_2$ with the weight ratio, $CuO:SiO_2$ ; 1:1. As shown in Fig. 3, the sulfate started to decompose above 650°C. Considering the purpose of "Low" temperature sorbent development, a big gap between sulfidation and regeneration temperature would be undesirable. Therefore, it is necessary to minimize sulfate formation by introducing a suitable additive.

**Effects of $SiO_2$ Contents**

To investigate effects of $SiO_2$ contents on sulfur loading, various sorbents, which have same metal oxide contents but different $SiO_2$ contents, were prepared. Because $SiO_2$ doesn't have desulfurization ability, sulfur loading decreased as $SiO_2$ contents in the sorbents increased. In preparing sorbents by the impregnation or precipitation method, their sulfur loading can be increased with small content of metal oxides. However, in this research where the simple physical mixing method was used, sorbents should contain at least 75wt% metal oxides content in order to keep its sulfur loading over 10wt%. If sorbents consist of 100wt% metal oxide, sulfur loading in a multicycle reaction would decrease because of calcination of metal oxide causing mass transfer inhibition. Effects of $SiO_2$ contents on sulfur loading are shown in Table 3.

**Table 3. Effects of silica on sulfur loading**

| Sorbent | Metal Oxide (wt%) | Silica (wt%) | $CuO:MoO_3:$ $MnO_2$ | Metal content (wt%) | Sulfur Loading (wt%) |
|---------|-------------------|--------------|----------------------|---------------------|----------------------|
| CMS2 | 27 | 73 | 71:25:4 | 20 | 4 |
| CMS1 | 50 | 50 | 71:25:4 | 37.88 | 8 |
| CMS4 | 75 | 25 | 71:25:4 | 56.9 | 12 |
| CMS5 | 100 | 0 | 71:25:4 | 75.93 | 16 |

**Effects of additives**

Sulfur loading of sorbents with various metal oxide contents and fixed silica content(25%) were studied to investigate effects of additives on sulfidation reaction. Table 4 shows the changes of sulfur loading of sorbents with various metal oxide contents. Results of sulfidation reaction with changing metal contents are shown in Fig. 4. As can be seen in Fig. 4 and Table 4, sulfur loading increases as metal oxide content increases. Effects of $MoO_3$ on sulfidation were negligible. It was expected that $MoO_3$ would play a role of promoter for sulfidation. However, its promoting effect was not identified in relatively short-term cyclic reactions of sulfidation/regeneration. CMS6 sorbent showed the most preferable sulfur loading.

**Table 4. Effects of additives on sulfur loading (TGA)**

| Sorbent | Metal Oxide (%) | Silica (%) | CuO:MoO3:MnO2 | Metal content (%) | Sulfur loading (%) |
|---------|-----------------|------------|---------------|-------------------|---------------------|
| CMS7 | 75 | 25 | 56:40:4 | 40.5 | 7 |
| CMS4 | 75 | 25 | 71:25:4 | 56.9 | 12 |
| CMS6 | 75 | 25 | 81:15:4 | 60.85 | 13 |
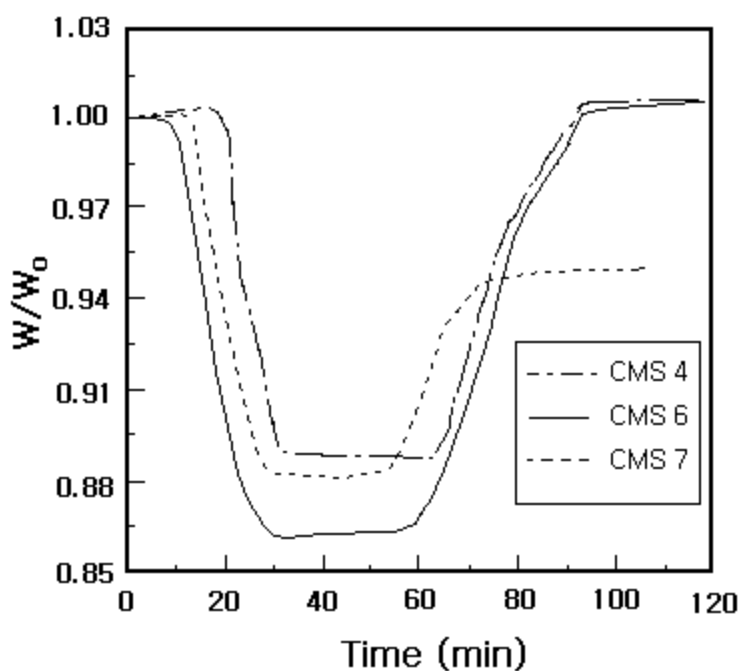


Fig. 4. Effect of additives on sulfur loading.

**Multicycle Reaction**

Since CMS 6 sorbent showed better sulfur loading than any other sorbent, it was tested in a GC/microreactor system in order to further investigate its sulfur loading in the multicycle reaction. The result of multicycle reaction for CMS 6 sorbent is shown Fig. 5. As shown in the figure, the breakthrough time increases as the cycle number increases. This might be due to stabilization of sorbent as the reaction is repeated. The sorbent was fully stabilized over 15cycles and its sulfur loading was 15wt%, which is larger than that obtained from TGA experiment.

To investigate the effects of additives on long-term sulfidation/regeneration cyclic reaction, CS2 sorbent was prepared and tested in the microreactor system. As shown in Table 5, CS2 sorbent contains CuO and silica only.

**Table 5. Composition of CMS6 and CS2 sorbent**

| Sorbent | CuO:MoO$_3$:MnO$_2$:SiO$_2$ | Others : Silica | CuO:MoO$_3$:MnO$_2$ | Metal Content |
|---------|------------------------------|------------------|---------------------|---------------|
| *CMS6*  | 64:11:3:25                   | 75:25            | 81:15:4             | 61            |
| *CS2*   | 75:0:0:25                    | 75:25            | 100:0:0             | 75            |
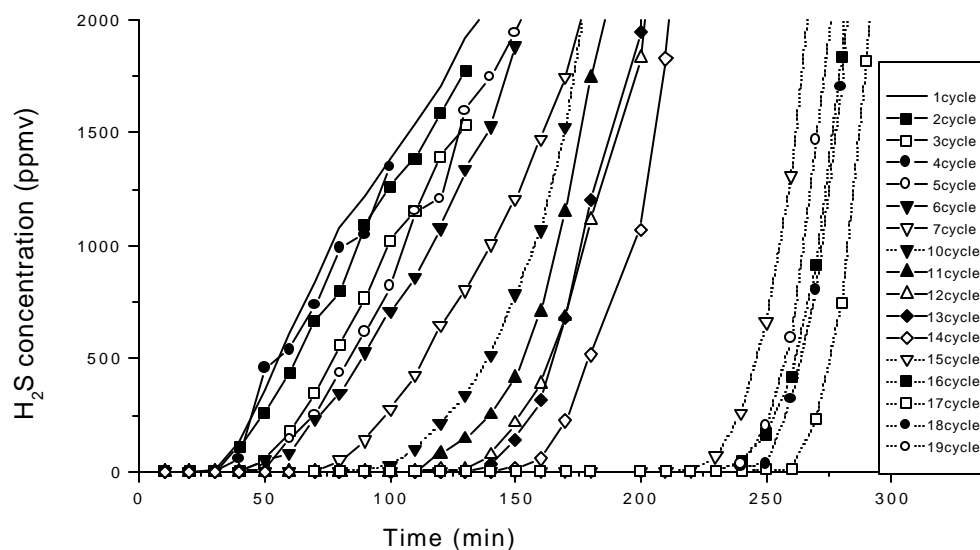


**Fig. 5. Breakthrough curves of CMS6.**

The result of multi-cycle reaction for CS2 sorbent in the microreactor is shown Fig. 6. As shown in the figure, the breakthrough time little increased as cycle number increased. Compared to CMS 6 sorbent, its breakthrough time increment was very small, implicating that additives(MoO$_3$ and MnO$_2$) do not affect sulfidation efficiency significantly. However, MoO$_3$ and MnO$_2$ can give a positive effect on sulfur loadings. Sulfur loadings of CMS6 and CS2 sorbents are shown in Fig. 7 and Fig. 8. Sulfur loading was calculated based on the outlet H$_2$S of 50ppm. Fig. 5 and Fig. 6 showed exactly same trend with breakthrough curves of CMS6 and CS2 sorbents. Before the 5th cycle, the sulfur loading of CS2 sorbent was almost twice of that of CMS6 sorbent. However, after the 19th cycle in which sorbents were believed to be fully activated, sulfur loading of CMS6 sorbent became larger than that of CS2 sorbent. This result confirms that CMS6 sorbent containing additives (MoO3 and MnO2) shows better result than any other sorbent.
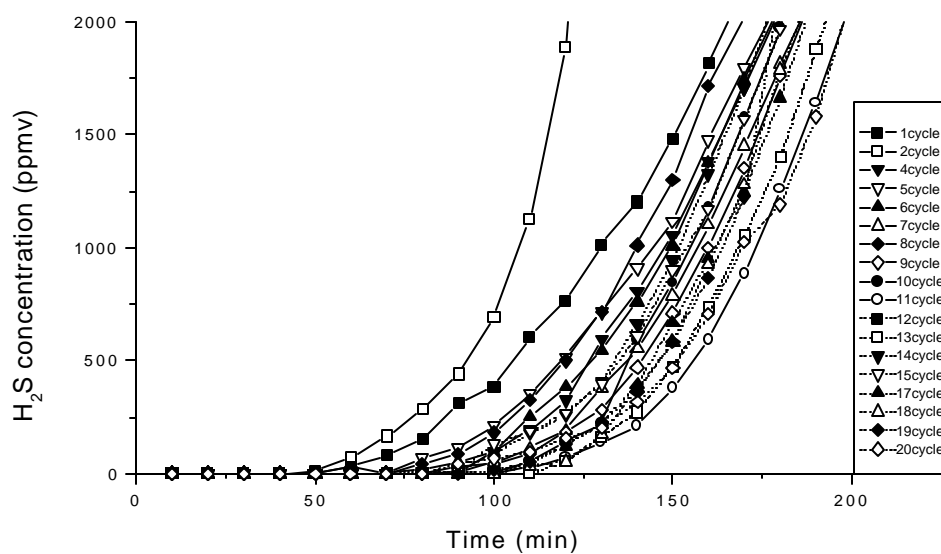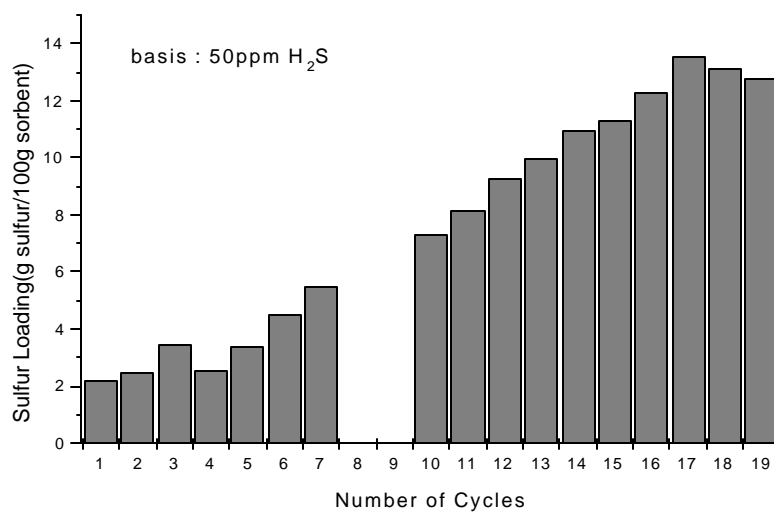
**Fig. 6. Breakthrough curves of CS2.**



**Fig. 7. Sulfur loading change of CMS6 in cyclic reaction.**
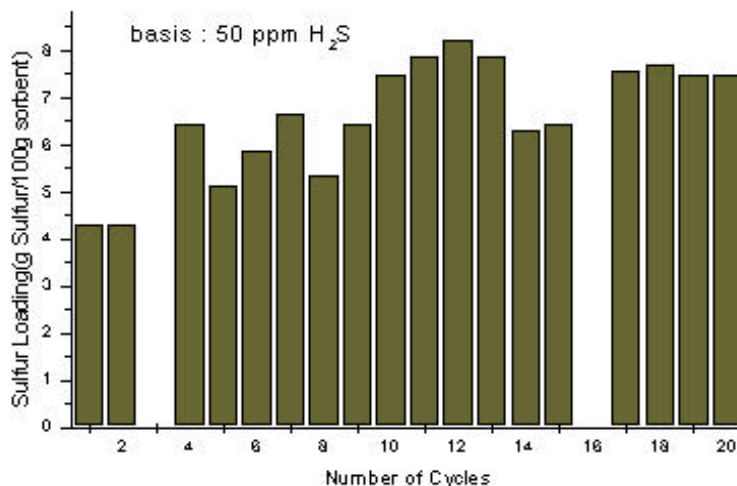
**Fig. 8. Sulfur loading change of CS2 in cyclic reaction.**

## CONCLUSION

Various sorbents were prepared by simple mixing method. CuO was used as main active material, $MnO_2$ and $MoO_3$ as additives, and $SiO_2$ as support material. TGA screening and GC/microreactor multi-cycle reactions were carried out to characterize reactivities of sorbents. Sulfidation temperature was 500 and regeneration temperature ranged 500~700 .

Promoting effect of $MoO_3$ on sulfidation reaction was not observed in the TGA experiment, but it was significant in the multi-cycle reaction. To keep the sulfur loading of sorbent over 10%, $SiO_2$ content in the sorbents should be below 25wt%.

In the GC/microreator multicycle reaction, $H_2S$ breakthrough time of CMS6 sorbent increased as the cycle number increased. It is inferred that this be due to stabilization of the sorbent structure. CMS6 sorbent containing additves of $MoO_3$ and $MnO_2$ was fully stabilized after the 19th cycle and its sulfur loading was 15%. However, $H_2S$ breakthrough time of CS2 sorbent which contains no additives increased little as the cycle number increased. So far, CMS6 sorbent turns out to have the most promising metal oxide combination of CuO, $MnO_2$ and $MoO_3$.

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